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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LATEX POLYMER BASED PRINTING INK

(57) Abstract: A latex polymer based ink comprising: (a) water; (b) a latex polymer; (c) pigment; (d) an acid neutralization agent; and (e) a rewetting agent. Alternative embodiments may include a modified rosin polymer, non-ionic surfactant and adjuvants.

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## LATEX POLYMER BASED PRINTING INK

### Field of the Invention

The invention relates to latex polymer based printing ink.

### Description of Related Art

In an attempt to eliminate volatile organic compounds (VOCs) in the pressroom, water-based alternatives are being sought for ink formulations. Water-based printing inks for use in flexographic printing processes are known in the prior art. This type of printing process utilizes printing plates wherein the printing images stand up in relief, i.e. the areas to be printed are raised above the non-printing areas. Printing by the flexographic process requires relatively low pressure while sufficient pressure is applied to transfer the ink from the face of the image carrier to the surface of the substrate. Examples of useful water-based flexographic printing inks are disclosed in U.S. Patent No. 4,173,554 and The Printing Ink Manual, edited by R.H. Leach and R.J. Pierce, pages 571-576, 5th edition, (Blueprint, 1993).

Water-based inks for gravure printing are also well known. In the gravure process, the printing image is engraved into a cylinder in the form of cells which become filled with ink. Printing is achieved by passing the substrate between the gravure cylinder and impression roller under pressure. Examples of useful water-based gravure printing inks are disclosed in U.S. Patent Nos. 4,954,556 and 5,098,478.

The offset lithographic printing process presents a unique challenge to ink formulators since such process utilizes a planographic printing plate, i.e. the image and non-image areas are in the same plane on the image carrier, and two fluids are concurrently utilized.

It is fairly simple to define an image area by raising it above the background as in the case of the flexographic printing plate or lowering it as in the case of the gravure printing plate; avoidance of ink adhering to the non-image area is not too difficult to achieve. However, when all areas are on the same level, techniques must be utilized to insure that ink adheres only to the image area, and not to the non-image area.

In conventional offset lithographic printing processes, the plate is damped before it is inked with an oil-based ink. Typically, the damping process utilizes a fountain solution such as those described in US patents 3,877,372, 4,278,467 and 4,854,969. Water will form a film on the hydrophilic areas (i.e. the non-image areas) of the printing plate, but will contract into tiny droplets on the oleophilic areas (i.e. the image areas). When an inked roller containing the oil-based ink is passed over the damped plate, it will be unable to ink the areas covered by the water film (the non-image areas), but will emulsify the droplets on the water-repellant areas (the image areas) and these will ink up. Such process is called offset lithography because the inked image on the plate does not directly print onto the paper substrate, but is first "offset" onto a rubber blanket, and transferred therefrom onto the paper substrate.

As mentioned above, conventional offset lithographic printing processes entails the use of oil-based inks and water-based fountain solutions. The ink/water balance is critical and is quite demanding of the pressman's skills. This issue is one of the several disadvantages associated with such printing processes as compared to flexographic and gravure printing processes. Moreover, the oil-based inks and aqueous fountain solutions typically employed in conventional offset lithographic printing processes contain fairly high levels of undesirable volatile organic compounds ("VOCs").

U.S. Patent 3,356,030 discloses the use of a water-based printing ink in respect to a method of planographic printing utilizing a lithographic printing plate whose non-image areas are coated with a cured coating of a thermosetting silicone resin. However, the patented method also entails the use of a volatile hydrocarbon fountain solution which will coat the non-image areas and which is re-applied between successive printings. Of course, the use of a volatile hydrocarbon fountain solution

undermines the principal purpose of the water-based ink compositions of the present invention, i.e. the avoidance of the use of volatile organic compounds ("VOCs") during the printing process. Indeed, the water-based ink compositions of the present invention may be used for offset lithographic printing processes without any fountain solution whatsoever.

In the 1980s, a resurgence of interest occurred in respect to "waterless" lithographic printing processes. Both positive and negative waterless planographic printing plates are commercially available from Toray Industries of Japan. The image area of a waterless planographic plate is a photopolymer similar to that employed for the image area of a conventional plate. However, the non-image area is coated with a polymer such as a silicone which is ink repellent. Further information about waterless printing plates and processes may be found in U.S. Patents 5,370,906 and 5,417,749.

The waterless printing process solved two issues: VOCs emanating from the fountain solutions and control of the ink/water balance by the pressman. However, the difference in surface energy between the image and non-image areas of the conventional offset lithographic printing plate is typically 40 dynes/cm is dramatically reduced to 20 dynes/cm in the case of the waterless printing plate. Therefore the latitude between scumming and poor print density is considerably narrowed and the issue of VOCs (emanating from the oil-based ink) still remains in respect to waterless printing.

German Offenlegungsschrift DE 41 19 348 A1 pertains to a moistureless offset printing method and a water-based printing ink. The ink described therein is one which will adhere to hydrophilic materials, but not to hydrophobic materials, and contains a dye, water, 5-50% water-soluble macromolecular binder and a hygroscopic liquid, preferably a multihydric alcohol.

U.S. Patent 5,725,646 disclosed an invention eliminating the principal disadvantages of conventional offset lithographic printing inks, viz. high levels of VOCs emanating from the oil-based ink and the aqueous fountain solution and the difficulty in controlling the ink/water balance, while preserving the principal advantage of the conventional lithographic printing process, i.e. high surface energy differential between the image and non-image areas of the printing plate.

U.S. Patent 5,725,646, teaches a method for making a water based offset lithographic printing ink based predominantly on a rosin ester salt (neutralized to be in a pH range of 7.5-10). Smaller amounts of aqueous emulsion polymers (0-20%) were also present. That invention comprised a water-based printing ink, based predominantly on a rosin ester salt, that is to be used in offset lithographic newspaper printing processes without the need for any accompanying fountain solutions.

While the method described in U.S. Patent No. 5,725,646 is satisfactory up to a press speed of 1,000 feet per minute, the method is not optimal for higher print speeds. For faster printing speeds up to 3,000 feet per minute, the rosin salts do not release the neutralizing amines fast enough for drying to occur. Additionally, large quantities of the modified rosin salts result in unacceptably high tack for high speed printing. Although a lower tack of the composition can be obtained by increasing the emulsion polymer content beyond 20%, an unacceptable drying up on conventional offset press ink trains, e.g., typically containing 5 or more transfer rolls, will occur.

An object of the present invention is to provide a fast drying offset lithographic printing ink which eliminates the disadvantages of present water based lithographic printing inks by permitting fast drying for acceptable high speed printing.

#### General Description of the Invention

It has been found that it is possible to incorporate large amounts of certain latex polymers and reduce the use of soluble resins thus obtaining fast drying waterbased offset inks. These compositions are stable on conventional ink trains. The general requirement for these class of latex polymers seems to be a particle size average of less than .03 micron, preferably 01. to 0.2 micron.

The invention generally comprises a latex polymer based ink comprising:

(a) water; (b) a latex polymer; (c) pigment; (d) an acid neutralization agent; and (e) a rewetting agent.

In another embodiment, a modified rosin polymer may be included. The modified rosin polymer may be comprised of: (i) resin soluble in water regardless of the pH of the water, (ii) resin rosin salts soluble in water at a pH ranging from about 7.5 to about 10, and (iii) aqueous emulsions resins.

### Detailed Description of the Invention

The printing plates for use with the newspaper printing ink of the present invention should be such that the image areas thereof are hydrophilic in nature, while the non-image areas are hydrophobic in nature. An example of a suitable printing plate is the "waterless" Toray type discussed above. However, the image area of the plate need not contain a photopolymer. The image area of the plate may comprise, e.g. a grained aluminum surface which has no coating thereon, but is hydrophilic in nature. The non-image area of the plate must, of course, be hydrophobic in nature. However, the non-image area may be covered with any type of hydrophobic material, provided that such hydrophobic material adheres to the non-images area of the plate during the printing process.

The latex polymers employed in the present invention are those of a particle sign of less than .03 micron. Preferably, the particle size of the latex polymers is 0.1 to 0.2 micron. Suitable examples of such latex polymers are urethane latex polymers or acrylic latex polymers such as an acrylic latex polymer from S. C. Johnson Joncryl 537.

The pigment may be any of those which are suitable for formulating offset lithographic printing inks such as CI Pigment Yellows 1, 3, 4, 5, 12, 13, 14, 17, 55, 65, 73, 83, 97 and 98; CI Pigment Oranges 13, 16 and 46; CI Pigment Reds 2, 3, 4, 10, 12, 48, 48:1, 48:2, 53, 57:2, 81, 104, 146, 170 and 176; CI Pigment Greens 2, 7 and 36; CI Pigment Blues 1, 15:1, 15:2, 15:3, 15:6, 16, 29, 56 and 61; CI Pigment Violets 3, 23 and 37; CI Pigment Blacks 6 and 7; and CI Pigment Whites 6, 7, 18 and 26.

Examples of rewetting agents for water based printing inks are well known in the art and may be employed in accordance with the present invention, however, the preferred rewetting agent is hydroxyethylethylene urea. Similarly, examples of acid neutralization agents for use in water based printing inks are equally well known in the art, however, the preferred acid neutralization agent is monoethanolamine.

The modified rosin polymer according to the present invention may be a maleic modified rosin esterified with pentaerythritol. Examples of suitable modified rosin polymers which are soluble in the water phase of the ink regardless of the pH of the water phase include: carboxymethyl-cellulose, hydroxyethylcellulose, hydroxypropyl-cellulose, hydroxybutylmethylcellulose, poly(C<sub>1</sub>-C<sub>4</sub>) alkylene oxides, polyethyleneimine, polyvinyl alcohol, polyvinyl acetate, polyvinylpyrrolidone, polyvinyl-oxazolidone and polyacrylamide polymers.

Preferably, the modified rosin polymers present in the ink are only those modified rosin polymers which are soluble in the water at pH ranging from about 7.5 to about 10. Suitable examples of such resin rosin salt binders include methacrylic resins; styrene-acrylic resins; rosin salts; and polystyrene- sulfonic acid and their salts. Ammonia or an organic amine such as monoethanolamine or N,N-diethanolamine may be added to the water phase in order to adjust the pH to the preferred value (a mineral acid or an organic acid such as acetic acid may be used to adjust the pH to a value in the range of about 2.5 to about 6.5).

Suitable examples of the modified rosin polymers comprising aqueous emulsions include acrylic or vinyl emulsion polymers prepared from monomers selected from the group consisting of acrylic acid esters, methacrylic acid esters, acrylic acid esters of polyhydric alcohols, methyl methacrylate, styrene, vinyl styrene and vinyl acetate.

In the latex polymer based printing ink of the present invention the water is present in amounts of 25 to 60 wt.%; and more preferably 35 to 50 wt.%. The latex polymer is present in amounts of 10 to 50 wt.%, and more preferable 15 - 40 wt.%. The pigment is present in amounts of

10 to 25 wt.%. The acid neutralization agent is present in amounts of 0.5 - 2 wt.%. Finally, the rewetting agent is present in amounts from 0.5 to 10 wt.%. It is also preferred that when a modified rosin polymer is used, it be present in amounts of 10 to 70 wt.%; and more preferably 30 to 60 wt.%; and most preferably the macromolecular resin binder is a composite having up to 5 wt.% of a resin binder soluble in water regardless of the pH of the water; 10 to 70 wt.% of a resin binder soluble in water at a pH ranging from 7.5 to 10; and up to 20 wt.% of an aqueous emulsion resin binder.

If desired, the usual adjuvants such as waxes, anti-foam agents, biocides, surfactants, corrosion inhibitors, etc. may be incorporated in the inks of the present invention. In a preferred embodiment of the water-based offset lithographic printing ink of the present invention a non-ionic surfactant is employed in the amount of up to 5 wt.%. Suitable examples of the surfactant include acetylenic glycols, ethoxylated glycols and sorbitan esters.

The latex polymer based printing ink of the present invention are further illustrated by the following non-limiting examples in which all parts and percentages are by weight, unless otherwise indicated.

#### Example 1

A black water based offset ink was prepared as follows, and made with the following compositions:

Carbon black	40%
Water soluble alkyl	35
Surfynol 420	3
Hydroxyethyl ethylene urea (75% solids)	20
Monoethanol amine	<u>2</u>
Total:	100%



From the above formulation, a water based ink was made as follows:

Black base	50%
Urethane Latex polymer	30%
Modified Rosin polymer	<u>20%</u>
Total:	<u>100%</u>

The latex polymer was a urethane type containing 40% solids and 60% water. The composition was stable on a conventional ink train on a Heidelberg press and gave dry prints comparable to magic oil based inks. In addition, the ink was easily washed off from the press rollers with plain tap water.

#### Example 2

A black water based offset ink was prepared as follows, and made with the following compositions:

Carbon black	40%
Water soluble alkyl	35
Surfynol 420	3
Hydroxyethyl ethylene urea (75% solids)	20
Monoethanol amine	<u>2</u>
Total:	100%

From the above formulation, a water based ink was made as follows:

Black base	50%
Acrylic Latex polymer	30%
Modified Rosin polymer	<u>20%</u>
Total:	<u>100%</u>

A composition similar to Example 1 was made replacing the urethane latex polymer with an acrylic latex polymer from S.C. Johnson Joncryl 537.

The latex polymer was an acrylic type from S.C. Johnson having the trade name Joncryl 537. The composition was stable on a conventional ink train on a Heidelberg press and gave dry prints comparable to magic oil based inks. In addition, the ink was easily washed off from the press rollers with plain tap water.

The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements on the invention that fall within the scope and spirit of this invention as set forth in the following claims.

## WHAT IS CLAIMED IS:

1. A latex polymer based printing ink comprising: (a) water; (b) a latex polymer; (c) a pigment; (d) an acid neutralization agent; and (e) a rewetting agent.
2. The ink of claim 1, wherein the amount of water present is 25 to 60 wt.%.
3. The ink of claim 1, wherein the amount of latex polymer present is 15 to 40 wt.%.
4. The ink of claim 3, wherein the latex polymer is a urethane latex polymer.
5. The ink of claim 3, wherein the latex polymer is an acrylic latex polymer.
6. The ink of claim 1, wherein the amount of pigment present is 10 to 25 wt.%.
7. The ink of claim 1, wherein the pigment is selected from the group consisting of CI Pigment Yellows 1, 3, 4, 5, 12, 13, 14, 17, 55, 65, 73, 83, 97 and 98; CI Pigment Oranges 13, 16 and 46; CI Pigment Reds 2, 3, 4, 10, 12, 48, 48:1, 48:2, 53, 57:2, 81, 104, 146, 170 and 176; CI Pigment Greens 2, 7 and 36; CI Pigment Blues 1, 15:1, 15:2, 15:3, 15:6, 16, 29, 56 and 61; CI Pigment Violets 3, 23 and 37; CI Pigment Blacks 6 and 7; and CI Pigment Whites 6, 7, 18 and 26.
8. The ink of claim 6, wherein the pigment is selected from the group consisting of CI Pigment Yellows 1, 3, 4, 5, 12, 13, 14, 17, 55, 65, 73, 83, 97 and 98; CI Pigment Oranges 13, 16 and 46; CI Pigment Reds 2, 3, 4, 10, 12, 48, 48:1, 48:2, 53, 57:2, 81, 104, 146, 170 and 176; CI Pigment Greens 2, 7 and 36; CI Pigment Blues 1, 15:1, 15:2, 15:3, 15:6, 16, 29, 56 and 61; CI Pigment Violets 3, 23 and 37; CI Pigment Blacks 6 and 7; and CI Pigment Whites 6, 7, 18 and 26.
9. The ink of claim 1, wherein the amount of acid neutralization agent present is 0.5 to 2 wt.%.

10. The ink of claim 1, wherein the acid neutralization agent is monoethanolamine.
11. The ink of claim 9, wherein the acid neutralization agent is monoethanolamine.
12. The ink of claim 1, wherein the amount of rewetting agent present is 0.5 to 10 wt. %.
13. The ink of claim 1, wherein the rewetting agent is hydroxyethyl ethylene urea.
14. The ink of claim 12, wherein the rewetting agent is hydroxyethyl ethylene urea.
15. The ink of claim 1, further comprising a modified rosin polymer comprised of: (i) resins soluble in water regardless of the pH of the water, (ii) resin rosin salts soluble in water at a pH ranging from about 7.5 to about 10, and (iii) aqueous emulsion resins; (c) a soybean oil based resin; (d) pigment; (e) a hydroxyethylethylene urea rewetting agent; (f) a latex polymer.
16. The ink of claim 15, wherein the modified rosin polymer soluble in the water regardless of the pH of the water are selected from the group consisting of carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxybutylmethylcellulose, poly(C<sub>1</sub>-C<sub>4</sub>)alkylene oxides, polyethyleneimine, polyvinyl alcohol, polyvinyl acetate, polyvinyl-pyrrolidone, polyvinylloxazolidone and polyacrylamide.
17. The ink of claim 16, wherein the macromolecular resin binders soluble in the water at a pH ranging from about 7.5 to about 10 are selected from the group consisting of methacrylic resins; styreneacrylic resins; rosin salts; and polystyrenesulfonic acid and corresponding salts.
18. The ink of claim 15, wherein the macromolecular resin binders comprising aqueous emulsions are selected from the group consisting of acrylic or vinyl emulsion polymers prepared from monomers selected from the group consisting of acrylic acid esters, methacrylic acid

esters, acrylic acid esters of polyhydric alcohols, methyl methacrylate, styrene, vinyl styrene and vinyl acetate.

19. The ink of claim 1, further comprising a non-ionic surfactant

20. The ink of claim 19, wherein the non-ionic surfactant is present in an amount of up to 5 wt.%.

21. The ink of claim 20, wherein the nonionic surfactant is selected from the group consisting of acetylenic glycols, ethoxylated glycols and sorbitan esters.

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# INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 33757 A (SUN CHEMICAL CORP ;HEIDELBERG HARRIS INC (US)) 18 September 1997 (1997-09-18) claims 5-16 example 1	1,2,5-21
X	WO 99 27022 A (SUN CHEMICAL CORP) 3 June 1999 (1999-06-03) claims 1-13	15-21
X	WO 97 33944 A (SUN CHEMICAL CORP) 18 September 1997 (1997-09-18) cited in the application claims 1-13	15-21
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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